ACTION OF HEAT AND MOISTURE ON LEATHER*

IV. THE EFFECT OF CHROME CONTENT AND DETANNAGE BY SODIUM LACTATE ON THE RESISTANCE OF CHROME LEATHER TO MOIST HEAT

ABSTRACT

Damage to chrome leather in wear is probably due to the combined action of the constituents of perspiration and the action of moist heat.

Chrome leather was treated with various concentrations of sodium lactate to reduce its chrome content to values in the range 5.0–0.5% Cr_2O_3. A series of leathers of varying chrome contents was also prepared using similar basic chromic sulfate liquors.

Detannage by sodium lactate solutions had relatively little effect on the chrome leather but reduced its resistance to the action of moist heat (40°C. and 100% r.h.).

Damage was slight down to 3.0% Cr_2O_3, and then increased rapidly with further fall in the chrome content. Although appearance and feel indicated extensive damage, the strength of the leathers as measured by buckle tear loads was not reduced.

The leathers tanned directly to corresponding chrome contents were much less affected. The shrinkage temperatures of these leathers was higher, and this appears to be the more important factor governing deterioration.

Damage appears to be primarily due to hydrolytic breakdown of the protein and loss of molecular structure. The presence of stabilizing cross links due to chrome tanning slightly reduces hydrolytic breakdown, but what is perhaps more important, it reduces loss of molecular structure even if such breakdown does occur. A very small amount of chrome, e.g., 0.3% Cr_2O_3, can exert a stabilizing effect provided it all contributes to tanning.

It is concluded that deterioration in wear is primarily due to the action of moist heat. Perspiration by reason of the lactate ions

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present causes detannage and so reduces the resistance of the leather to such conditions. The accumulation of salts from the perspiration in the leather, leading to increased water absorption, is probably a contributory factor.

INTRODUCTION

The damage caused to chrome leather by perspiration is generally ascribed to the detanning action of the lactate ions present (1,2), the rise in pH which results from the absorption of the perspiration being a contributory factor (3,4).

Treatment with synthetic perspiration, however, appears to have little effect on the strength of chrome leather (5), and although the leather becomes rather thinner and less supple, it does not appear excessively damaged unless the chrome content is severely reduced.

Chrome leather is also relatively unaffected by exposure to moist heat at 40°C. (6,7), and only under some circumstances have severe losses of strength been recorded (2,8,9). It seems probable that damage in wear is due to the combined action of the chemical constituents of perspiration and the action of moist heat, detannage by the lactates, and the rise in pH due to the absorption of the perspiration reducing the resistance of the leather to the warm moist conditions accompanying its production.

In order to obtain further information on this point, the chrome content of a leather has been reduced to various levels by treatment in sodium lactate solutions, and its subsequent behavior on storage over water at 40°C. has been examined and compared with that of leathers tanned directly to a similar range of chrome contents.

EXPERIMENTAL

The raw material for these experiments was a pickled grain hide split and a chrome-tanned side, both prepared by normal commercial processes. The chrome side was tanned in a basic chromic sulfate liquor and acetone-dehydrated. Acetone-dehydration was used throughout so that the leather would be dried out in a satisfactory condition without the complications due to added fatliquors.

Experiment I

Six blocks 6″ x 18″ were cut from the chrome side and subdivided into twelve samples 6″ x 1.5″, all cut with their long side at right angles to the backbone. One sample from each block was allotted to each of the twelve treatments listed below.

The six samples to be given any one treatment were immersed in the appropriate solutions for 48 hours at room temperature using 18 ml. solution per g. leather.

1. 5% NaCl
2. 0.5% sodium lactate + 5% NaCl
3. 1.0% " " " " "
4. 1.5% " " " " "
5. 2.0% " " " " "
6. 2.5% " " " " "
7. 3.5% " " " " "
8. 4.8% " " " " "
9. 6.5% " " " " "
10. 10.0% " " " " "
11. 16.0% " " " " "
12. 30.0% " " " " "

The concentrations to be used in order to reduce the chrome content to a suitable range of values between 5% and 0.5% Cr_2O_3 were determined in a preliminary experiment.

The samples were washed in six changes of water and acetone-dehydrated.

Experiment II

Eight blocks 6″ x 8″ were cut from the pickled side in the same way as in Experiment I, and one sample from each was tanned at each level of chrome.

Tannage was carried out in a 2:1 float of a 33% basic chromic sulfate liquor to which 4% w/v Na_2SO_4 was added. The amounts of chrome offered varied between 0.1% and 1.4% Cr_2O_3 on pickled weight. The pieces were drummed in the liquor for 2 hours, left overnight, drummed for a further 2 hours, and then basicified to pH 4.0–4.2 with sodium bicarbonate over a period of 4 hours. A further set of samples obtained from a similar pickled hide split were also tanned (IIB). The samples were washed in several changes of tap water, the hardness of which was sufficient to give a light neutralization, and acetone-dehydrated.

Testing of leathers

In both experiments the strength (buckle tear load) (10) was determined on each sample. The torn pieces were cut off and chrome content (perchloric acid oxidation) (10), shrinkage temperature (in 75% v/v glycerol-water mixture) (11) and pH of water extract (2.5 g., in 50 ml.) were determined on the pooled samples from each treatment. The samples were then suspended over water in closed glass tanks at 40°C. A small beaker of toluene was included in each tank to discourage mold growth. After storage, the pieces were dried grain side downwards on glass plates.

Buckle tear load and shrinkage temperature were again determined. The percentage strength retained was calculated for each individual sample, and the average values for the six replicate samples in each treatment is recorded. Stiffness (modified lastometer) (12) and indentation index (10) were also determined on some samples.

Breakdown of the protein was assessed by determination of nitrogen soluble in 5*M* acetic acid (7) and by determination of amino groups liberated using fluorodinitrobenzene (13,14).

RESULTS

Experiment I

The treatments in lactate solutions caused little apparent damage to the leather. There was a slight decrease in thickness and an increase in stiffness with increasing concentration of lactate, and the leathers tended to become greener in color. The shrinkage temperature fell with the chrome content as indicated in Table I. The values were on the whole lower than those normally corresponding to the recorded chrome contents, suggesting that a proportion

TABLE I*

COMBINED EFFECT OF "PERSPIRATION" AND MOIST HEAT ON CHROME LEATHER

Leather Sample	Before Storage			After Storage					
	Chromic Oxide % Cr_2O_3	pH	Shrinkage Temperature, °C.	pH	Shrinkage Temperature, °C.	Strength % Retained†	Thickness % Retained*	Stiffness‡	Indentation Index**
Original leather	5.31		113						
1.	4.84	3.07	102	2.75	100	115	93	15	80
2.	4.16	3.98	100	3.26	104	126	97	8	80
3.	3.93	4.24	100	3.59	106	135	95	8	73
4.	3.13	4.52	92	5.82	96	118	91	75	70
5.	3.01	4.72	89	5.84	90	98	94	97	68
6.	2.77	4.83	80	6.75	87	118	90	97	74
7.	2.49	5.10	75	7.11	73	95	85	135	64
8.	1.81	5.72	68	7.60	70	95	79	280	52
9.	1.27	5.31	62	7.34	67	137	60	260	49
10.	1.17	5.44	61	8.36	67	143	47	300	23
11.	0.86	5.58	60	9.52	72	139	53	310	20
12.	0.56	5.70	61	9.36	74	146	55	380	20

*Reproduced from 1961 Annual Report.
†Buckle tear load after storage as percent buckle tear load before storage. Mean of six samples.
‡Modified Lastometer. Load in grams required to deflect the center of a 2" x 1" sample through 2 mm. Values increase with increasing stiffness (12).
**Indentation index determined as described in S.L.T.C. Official Methods 1957, p. 182. Values increase with increasing compressibility.

of the chrome remaining was complexed with lactate and not available as a tanning agent.

The leathers were examined at various times during storage. After three weeks, sets 1 to 4 still looked relatively dry, but the others appeared increasingly damper as the chrome content decreased, and sets 11 and 12 were quite wet and spongy in feel. The apparent greater water uptake was accompanied by darkening in color except with these last two sets which still remained light in color.

It was originally intended that the leathers should be stored for 6 months, but the samples of lowest chrome content appeared so damaged and spongy after thirteen weeks that it was decided to remove all the leathers. At this stage sets 1 to 4 still appeared relatively dry, 5 was slightly damp, 6 to 9 very damp, and 10 to 12 spongy and saturated with water. In spite of the toluene there was some mold growth on the samples in sets 6, 7, 8, and 9.

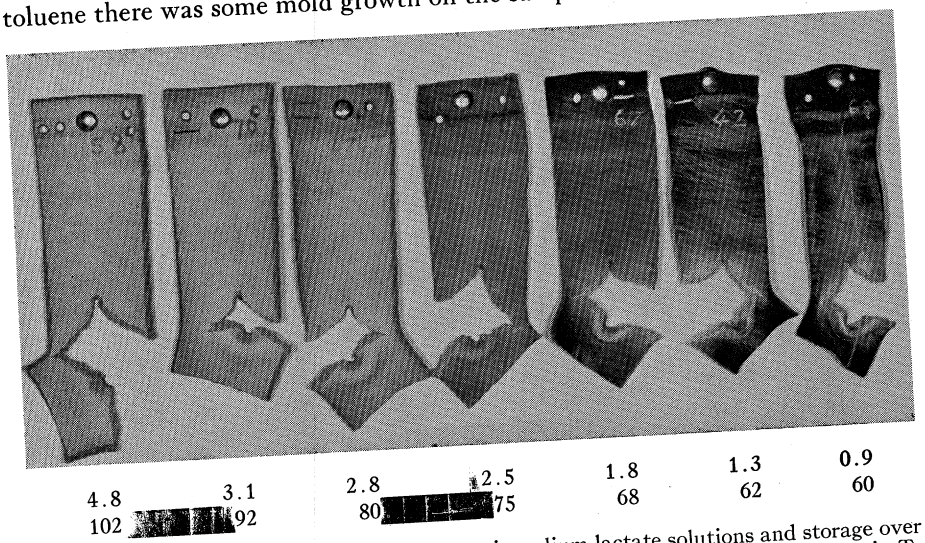


FIGURE 1—Chrome leathers after treatment in sodium lactate solutions and storage over water at 40°C. for 13 weeks. Top number is % Cr_2O_3; bottom number is Ts in °C.

After storage, the leathers tended to be thinner, stiffer and more papery in feel, and darker in color as the chrome content decreased (Fig. 1). Modified lastometer tests on a limited number of samples confirmed this increasing stiffness, and determination of indentation index showed that compressibility also decreased (Table I). These changes were relatively small down to about 3.0% Cr_2O_3, but they gradually became more pronounced at lower chrome contents until below 2.0% Cr_2O_3 the damage was very extensive, the samples being only half their original thickness, shrunken, and dark in color. Only the leathers of lowest chrome content were cracky, perhaps because of the high proportion of salts which they contained.

TABLE II

EFFECT OF STORAGE ON CHROME LEATHERS OF VARYING CHROMIUM CONTENT

Leather	Before Storage			After Storage					
	Cr_2O_3 %	T_s °C.	pH	T_s °C.	pH	Strength % retained*	Thickness % retained	Stiffness†	Indentation Index‡
Series A									
1.	3.36	103	3.38	109	3.12	90	91	260	50
2.	3.05	—		107		79	88	410	44
3.	2.75	—		104		90	98	370	62
4.	2.47	101		98	3.12	93	92	270	69
5.	2.02	97		97		85	92	230	61
6.	1.65	—		—		94	99	420	51
7.	1.40	90	3.68	89	3.32	98	97	370	50
8.	1.20	85		85		104	80	380	39
9.	0.84	81		81		97	76	490	39
10.	0.70	76		76	3.32	107	85	490	38
11.	0.30	68		62		90	85	600	24
12.	0.17	66	3.70	63	3.62	103	73	830	15
Series B									
1.	2.06	97	2.70	97	3.22	92	141	260	87
2.	1.82	93		90		89	125	—	—
3.	1.45	88	2.72	88	2.80	89	115	230	81
4.	1.18	85		84		87	111	450	43
5.	1.03	83		85		91	104	—	—
6.	0.63	75		74		88	125	380	55
7.	0.45	74	2.72	73	2.78	88	120	410	41
8.	0.22	65	2.75	69	2.89	91	133	750	35

*Buckle tear load after storage as percent buckle tear load before storage. Mean of six samples.
†Modified Lastometer. Load in grams required to deflect the center of a 2″ x 1″ sample through 2 mm. Values increase with increasing stiffness (12).
‡Determined as described in S.L.T.C. Official Methods 1957, p. 182. Values increase with increasing compressibility.

The poor appearance of the samples was not accompanied by any loss in strength as measured by the buckle tear test. If the decrease in thickness is taken into account, some of the leathers of low chrome content actually increased in strength by as much as 200–300%. This increase isd ifficult to explain. It is possibly due to the fact that, owing to shrinkage, there is a higher proportion of collagen per unit area, and also to the somewhat plastic nature of the samples. The effect of this on the way the leather tears can be seen in Fig. 1. After flexing in the hand for a few minutes, the samples of low chrome content could be readily torn along the flex line.

The shrinkage temperature generally increased during storage. The particularly large increases with leathers of low chrome content are probably due to partial shrinkage during storage and the difficulties of assessing the commencement of shrinkage.

The pH of most of the leathers increased during storage, the extent of this increase becoming progressively greater with the concentration of lactate used in stripping. This does not appear to be due to the production of ammonia, as the volatile-nitrogen extracted was relatively low (Table III). It might be due to replacement of hydroxyl ions in the chrome complex by lactate, but as the increases are greatest with the leathers of high chrome content, this does not appear to be a very likely explanation.

TABLE III

SOLUBILITY OF PROTEIN IN 5*M* ACETIC ACID

Nitrogen Extracted from Leathers after Storage as Percent Total Nitrogen

Experiment I

Leather	Nitrogen Extracted %	
	Volatile	Nonvolatile
No. 1, 4.8% Cr_2O_3	0.4	0.4
No. 12, 0.56% Cr_2O_3	0.3	11.7

Experiment IIA

Leather No.	Cr_2O_3, %	Total Nitrogen Extracted, %
1	3.36	0.26
5	2.02	0.14
6	1.65	0.16
11	0.30	0.32
12	0.17	1.10

Experiment IIB

Leather No.	Cr_2O_3, %	Total Nitrogen Extracted, %
1	2.06	0.17
5	1.03	0.36
7	0.45	0.46
8	0.12	1.18

Determination of free α-amino groups by reaction with fluorodinitrobenzene indicates that there is considerable hydrolytic breakdown of the protein in the samples of lowest chrome content (Table IV). This is also reflected in the increased solubility of the protein in 5*M* acetic acid (Table III). There is

some increase in α-amino groups in the leather of highest chrome content, but the solubility is not appreciably affected. Either the chrome reduces the extent to which hydrolytic breakdown occurs or else by reason of stabilizing cross links holds the collagen molecules together, so preventing access of fluorodinitrobenzene to free α-amino groups and disintegration of the protein in 5*M* acetic acid. Repeated stripping of leather from set No. 1 with sodium citrate before reaction with fluorodinitrobenzene had little affect on the number of α-amino groups detected (14). It would, therefore, appear that the first explanation is the more likely.

TABLE IV

DEGRADATION OF PROTEIN DURING MOIST STORAGE

Terminal Amino Groups Reacting with Fluorodinitrobenzene
Millimoles per 100 g. Hide Substance

Experiment I

Amino Acid Residue	Original Leather	Leather after Storage for 13 weeks at 40°C	
	5.31% Cr_2O_3	No. 1 4.84% Cr_2O_3	No. 12 0.56% Cr_2O_3
Aspartic acid	0.01	0.02	0.17
Glutamic acid	0.02	0.02	0.06
Serine	0.02	0.02	0.15
Threonine	0.02	0.03	0.48
Alanine	0.03	0.02	0.28
Glycine	0.07	0.10	0.90
Phenylalanine	0.05	0.09	1.21
Valine	0.02	0.04	0.34
Total	0.24	0.34	3.59
Mean weight per mole N-terminal residue	410,000	290,000	28,000

Experiment II

	Leather 1A		Leather 12A	
	Before 3.36% Cr_2O_3	After	Before 0.17% Cr_2O_3	After
Total α-amino groups	0.56	0.69	0.47	0.97
Mean weight per mole N-terminal residue	118,000	97,000	143,000	69,000

Storage did not lead to the liberation of any new terminal residues but only to increases in those present.

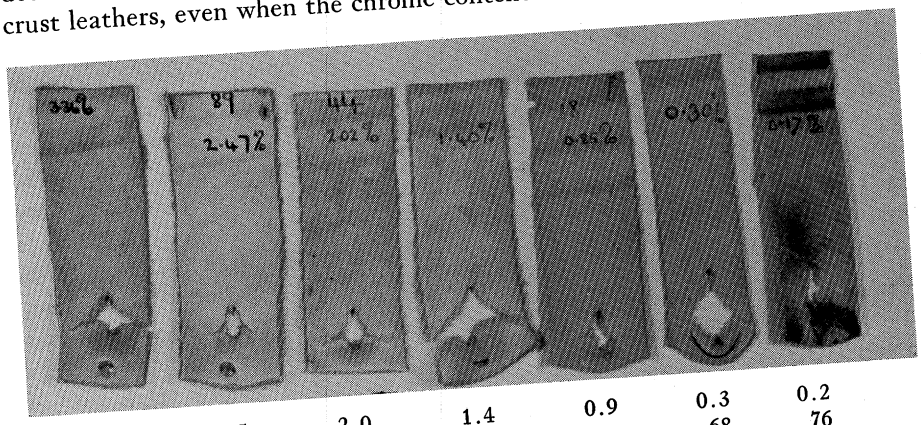
The high proportion of phenylalanine appearing as an end group in the leather of low chrome content is of interest.

Approximately one out of every 14 peptide bonds involving this amino acid is broken compared with one out of 354 in the case of glycine. It would seem that the peptide bond involving the amino group of phenylalanine is particularly labile.

Experiment II

In this experiment two batches of leather were tanned in basic chromic sulfate liquors to give a range of chrome contents between 0.2% and 3.4% Cr_2O_3 (Table II).

The color of the original leathers before storage was progressively paler as the chrome content decreased, and there was a tendency for stiffness to decrease. On the whole, however, the leathers were reasonably good for crust leathers, even when the chrome content was below 1.0%.



3.4	2.5	2.0	1.4	0.9	0.3	0.2
103	101	97	90	81	68	76

FIGURE 2—Leather tanned to varying chrome contents and stored over water at 40°C. for 13 weeks. Top number is % Cr_2O_3; bottom number is Ts in °C.

Storage over water at 40°C. led to relatively little change except for some general darkening and stiffening of the leathers of low chrome content (Fig.2). There was no indication of extensive water absorption during storage as in the first experiment, and altogether damage was very much less, although the chrome contents were in many cases appreciably lower. The shrinkage temperatures were, however, higher for corresponding chrome contents. In both experiments damage began to be obvious when the shrinkage temperature fell below about 90°C., and this appears to be the more important factor.

As in Experiment I there was no loss of strength as measured by buckle tear load, and the leathers were not cracky. Stiffness increased and compressi-

bility decreased with decrease in chrome content, but differences were much less than in the first experiment. Also, although the pH of water extracts of the leathers was lower than in the first experiment, protein breakdown, as assessed by solubility or by reaction with fluorodinitrobenzene, was very slight (Tables III and IV).

DISCUSSION

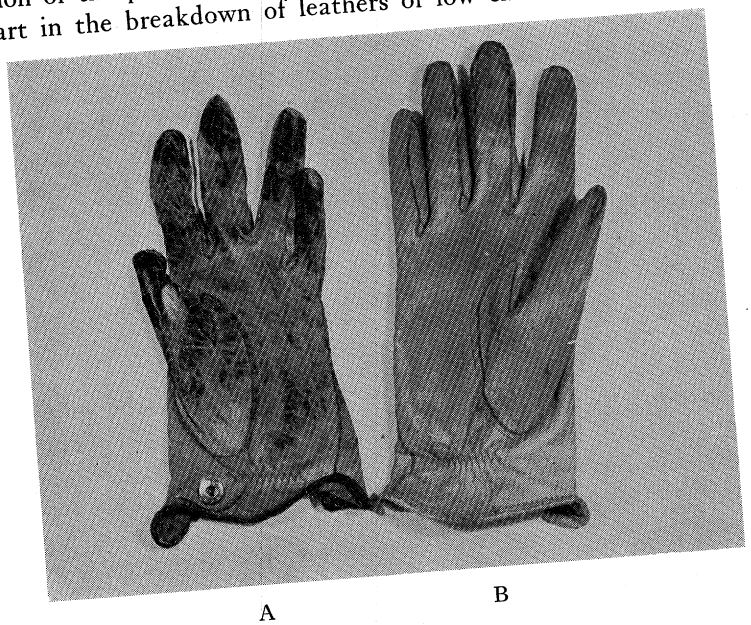
Although the appearance of a number of the leathers after moist storage indicated considerable damage had occurred, losses in strength as measured by buckle tear load were generally increased. Measurement of strength by this method is not, therefore, a reliable criterion of the breakdown occurring in such conditions. Since many of the leathers could be torn by hand after flexing, some method of test involving such mechanical action would appear to be preferable. As far as the present series of experiments are concerned, changes in appearance, thickness, and feel were taken as the main indications of breakdown.

The general inference to be drawn from this experiment is that detannage of chrome leather by lactate solutions, while in itself having little effect on the leather, reduces its resistance to the action of moist heat. Damage increases with the degree of detannage, slowly at first and then more rapidly as the chrome content falls below about 2.0 and the shrinkage temperature below 80°C. As stated above it is the appearance and feel of the leather which is mainly affected. Leathers tanned directly to corresponding chrome contents were much less damaged. This together with the much lower shrinkage temperature of the detanned leathers in relation to chrome content suggests that much of the chrome present in the detanned leathers is not functioning as a tanning agent but is probably present as a complex with lactate or, in view of the pH, precipitated as a basic salt. The extent to which deterioration occurs is more closely related to the shrinkage temperature than to the chrome content. In both series damage began to be apparent when the initial shrinkage temperature fell below about 90°C.—I 6, and II A7 and II B3—and becomes extensive when it falls below 70°C.

Even on the basis of similar shrinkage temperatures, however, the leathers detanned with lactate were more severely damaged than the leathers tanned directly to corresponding values. The "detanned" samples became quite damp during the moist storage, particularly those of low chrome content, due presumably to the sodium chloride and lactate present in these leathers. It seems likely that this higher moisture content allowed more extensive hydrolytic breakdown of the leathers (see below).

The appearance and feel of the detanned leathers 6 to 9 in Experiment I was similar to that of light-colored gloves and upper leathers damaged in wear (Fig. 3). The chrome contents and shrinkage temperatures were also typical of such leathers (Table V). There seems little doubt that the deterioration of

these leathers in wear is due to detannage by the lactate ions in perspiration followed by breakdown under the warm moist conditions associated with the production of the perspiration. The possibility that bacterial action plays some part in the breakdown of leathers of low chrome content cannot be



A B

FIGURE 3—Golf gloves damaged in wear.
A. Severe damage *B*. Slight damage

TABLE V

CHROMIUM CONTENT, SHRINKAGE TEMPERATURE, AND pH OF LEATHERS DAMAGED IN WEAR

Leather	Cr_2O_3, g. per 100 g. air-dry leather	Ts °C.	pH of water extract
Damaged gloves			
1.	0.88	68	—
2.	1.38	54	7.34
3.	1.50	62	5.10
Cracked upper leather			
1.	3.78	68	7.3
2.	—	71	6.5
3.	2.08	61	5.8
4.	2.15	66	7.3
5.	—	62	—
6.	—	93	6.8
7.	—	62	4.8

entirely excluded. The fact that there is little volatile-nitrogen produced suggests that it is small. Also, with collagen stored under comparable conditions there is little evidence of bacterial attack, and liberation of α-amino groups appears to be primarily due to chemical rather than bacterial breakdown (14).

In the present series of experiments damage to the leathers appears to be associated with liberation of α-amino groups. Such breakdown is small when the chrome content and shrinkage temperature are high, but on detannage with lactate it can become quite extensive. The absorption of moisture by reason of the high concentration of salts accumulating in the leather from perspiration is probably also a factor influencing breakdown.

The marked stabilizing effect of very small amounts of chrome is typified by Leather 12 in Experiment IIA with a chrome content of only 0.17% Cr_2O_3 and a pH of 3.4. Hydrolytic breakdown in this leather during storage was only about one tenth of that occurring with collagen of the same pH stored under comparable conditions for less than half the time (14). Solubility in 5*M* acetic acid was only 1.1%, whereas nearly 80% of the collagen was soluble in bicarbonate solution. The presence of even such small amounts of chrome appears to mitigate hydrolytic action probably by providing stabilizing cross links in the molecule and reducing access of water to the protein backbone. Perhaps what is more important from the point of view of damage, these stabilizing cross links prevent general loss of molecular structure even if hydrolytic breakdown does occur.

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